

Hexadecapolar Kondo effect in URu₂Si₂?

Anna I. Tóth and Gabriel Kotliar

Department of Physics & Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019, USA

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We derive the coupling of a localized hexadecapolar mode to conduction electrons in tetragonal symmetry. The derivation can be easily adapted to arbitrary multipoles in arbitrary environment. We relate our model to the two-channel Kondo (2CK) model and show that for an f^2 -configuration, a relevant crystal field splitting in addition to the 2CK interaction is intrinsic to tetragonal symmetry. We discuss possible realizations of a hexadecapolar Kondo effect in URu₂Si₂. Solving our model we find good agreement with susceptibility and specific heat measurements in Th_{1-x}U_xRu₂Si₂ ($x \ll 1$).

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Introduction. In an seminal paper [1], Cox addressed important differences between U- and Ce-based heavy electron materials in terms of the atomic structure of their f -shell. In Ce-based systems the most probable configuration has one f -electron, in contrast to many U-based materials having an f^2 -many body state as the most probable one. In crystal structures where the U-site has cubic symmetry, the f^2 -states can give rise to quadrupolar degrees of freedom which when coupled to conduction electrons lead to two-channel Kondo non-Fermi liquid behavior [1, 2]. Meanwhile various multipolar orderings have been observed [3] as well as proposed as candidates for “hidden order” (HO) in materials with clear phase transitions but without an obvious order parameter. A prominent example in this area is provided by URu₂Si₂. For this material quadrupolar [4], octupolar [5], hexadecapolar [6] and triakontadipolar [7] order parameters have all been put forth. Recent experiments have definitely ruled out quadrupolar order [8], whereas another might implicitly hint at it [9]. On the other hand, the hypothesis of active Uranium hexadecapolar degrees of freedom provides a natural explanation for numerous experiments [10]. In this Letter, we generalize the work of ref. [1] and present a simple construction of low-energy Hamiltonians that describe the coupling between multipoles and conduction electrons in the tetragonal crystal field of URu₂Si₂. We show that the U hexadecapolar degrees of freedom, couple symmetrically to multiple channels of conduction electrons. We solve the resulting model using the numerical renormalization group, and thereby successfully describe the properties of Th_{1-x}U_xRu₂Si₂ ($x \ll 1$) [12, 13]. Thus hexadecapolar fluctuations also serve as an explanation for the anomalies observed Th_{1-x}U_xRu₂Si₂ ($x \ll 1$).

Construction. To construct a tractable model, valid at very low-energies, we take into account only the two lowest-lying f -configurations with double occupancy. This is motivated by recent LDA+DMFT calculations which indicate that, while U has mixed valence in this material with f -electron occupancy between 2 and 3, two crystal field singlets with double occupancy and different symmetries have the highest probability [6].

The Uranium degrees of freedom are then described by a $J = 4$ multiplet, split by the tetragonal crystal structure. The ground state and the nearest excited level are, respectively, time-reversal and parity even, A_{2g} and A_{1g} basis states of the group $\mathcal{T} \times D_{4h}$ with $\mathcal{T} = \{\mathcal{I}, \mathcal{T}\}$ the group of time-reversal, \mathcal{I} the identity, \mathcal{T} the time-reversal operator; and D_{4h} the tetragonal point group including parity. Viz., the lowest-lying singlets are: $|A_{2g}\rangle \equiv \frac{i}{\sqrt{2}}(|4\rangle - |-4\rangle)$, and $|A_{1g}\rangle \equiv \frac{\cos\phi}{\sqrt{2}}(|4\rangle + |-4\rangle) + \sin\phi|0\rangle$, given in terms of the eigenvectors, $|J_z\rangle$, of the operator \hat{J}_z in the $J = 4$ multiplet with the quantization axis chosen parallel to the c -axis of the crystal. To keep the equations short, we follow refs. [1, 2] and assume, the f -shell of the U atom hybridizes predominantly with $l = 3, J = \frac{5}{2}$ conduction electrons. The conduction electrons at the local site, ψ_{lJz}^\dagger can be classified into the four double-valued or spinor irreducible representations (irreps), Γ_{6p}, Γ_{7p} of the tetragonal double point group, \bar{D}_{4h} , with $p = g/u$ for parity even/odd irreps (i.e. for l even/odd). Under time-reversal symmetry $\mathcal{T}\psi_{lJz}^\dagger\mathcal{T}^{-1} = (-)^{l-J+J_z}\psi_{lJ(-J_z)}^\dagger$. We set up a basis so that the $\alpha = \pm$ components of the Kramers doublets, $\Psi_{\Gamma_{jp}^{(n)}}^\dagger$ (where n enumerates doublets of the same type within the same J multiplet, and $j = 6, 7$) comply with our convention: $\mathcal{T}\Psi_{\Gamma_{jp}^{(n)}}^\dagger\mathcal{T}^{-1} = \Psi_{\Gamma_{jp}^{(n)}}^\dagger$, implying the same for annihilation operators. For the local conduction electron basis, we choose the following two independent Γ_{7u} Kramers doublets for creation operators:

$$\begin{bmatrix} \Psi_{\Gamma_{7u}^{(1)}}^\dagger + \\ \Psi_{\Gamma_{7u}^{(1)}}^\dagger - \end{bmatrix} \equiv \begin{bmatrix} \psi_{\frac{5}{2}}^\dagger \\ -\psi_{-\frac{5}{2}}^\dagger \end{bmatrix}, \quad \Psi_{\Gamma_{7u}^{(2)}}^\dagger \equiv \begin{bmatrix} \psi_{-\frac{3}{2}}^\dagger \\ -\psi_{\frac{3}{2}}^\dagger \end{bmatrix},$$

and one Γ_{6u} : $\Psi_{\Gamma_{6u}^{(1)}}^\dagger \equiv \begin{bmatrix} \psi_{\frac{1}{2}}^\dagger \\ -\psi_{-\frac{1}{2}}^\dagger \end{bmatrix}$, on using the condensed notation: $\psi_{J_z}^\dagger \equiv \psi_{3\frac{5}{2}J_z}^\dagger$. Adjoint doublets with the same transformation properties in the same basis are

$$\Xi_{\Gamma_{7u}^{(1)}} \equiv \begin{bmatrix} \psi_{-\frac{5}{2}} \\ \psi_{\frac{5}{2}} \end{bmatrix}, \quad \Xi_{\Gamma_{7u}^{(2)}} \equiv \begin{bmatrix} \psi_{\frac{3}{2}} \\ \psi_{-\frac{3}{2}} \end{bmatrix}, \quad \Xi_{\Gamma_{6u}^{(1)}} \equiv \begin{bmatrix} \psi_{-\frac{1}{2}} \\ \psi_{\frac{1}{2}} \end{bmatrix}.$$

Kondo Hamiltonians are made up of spin-flip and diagonal processes: $\mathcal{H}_K = \mathcal{H}_\perp + \mathcal{H}_z$. When constructing these two parts connecting the two singlets, the only relevant, non-trivial tensor products of irreps are $\Gamma_{6u} \otimes \Gamma_{6u} = \Gamma_{7u} \otimes \Gamma_{7u} = A_{1g} \oplus A_{2g} \oplus E_g$ and $A_{2g} \otimes A_{2g} = A_{1g}$ [15]. Inserting the appropriate tetragonal Clebsch–Gordan coefficients, symmetry thus binds the most general form for the spin-flip and diagonal parts to be [15]

$$\mathcal{H}_\perp = i \sum_{n,m=1}^2 \mathcal{J}_\perp^{nm} \left(\Psi_{\Gamma_{7u}^{(n)}+}^\dagger \Xi_{\Gamma_{7u}^{(m)}-} + \Psi_{\Gamma_{7u}^{(n)}-}^\dagger \Xi_{\Gamma_{7u}^{(m)}+} \right) \times |A_{1g}\rangle\langle A_{2g}| + h.c., \quad (1)$$

$$\mathcal{H}_z = \sum_{n,m=1}^2 \sum_{i \in \{1,2\}} \mathcal{J}_z^{nm i} \times \left(\Psi_{\Gamma_{7u}^{(n)}+}^\dagger \Xi_{\Gamma_{7u}^{(m)}-} - \Psi_{\Gamma_{7u}^{(n)}-}^\dagger \Xi_{\Gamma_{7u}^{(m)}+} \right) |A_{ig}\rangle\langle A_{ig}|. \quad (2)$$

The couplings are real and must satisfy $\mathcal{J}_z^{12i} = \mathcal{J}_z^{21i}$ to ensure hermiticity, but otherwise arbitrary. We omitted processes including Γ_6 electrons as they decouple from the impurity. The hexadecapolar, i.e. “spin-flip” fluctuations are thus coupled to four species of conduction electrons, namely to the two independent Γ_{7u} Kramers doublets. \mathcal{H}_\perp has the structure of the two-channel Kondo (2CK) model where the role of spin index is played by the index that distinguishes the two different Γ_{7u} ’s, and the channels are distinguished by the Kramers indices. To make this correspondence more explicit, we introduce the operators: $\begin{bmatrix} \eta_{a\uparrow} \\ \eta_{a\downarrow} \end{bmatrix} \equiv \begin{bmatrix} \psi_{-\frac{3}{2}} \\ \psi_{\frac{5}{2}} \end{bmatrix}$, $\eta_b \equiv \begin{bmatrix} \psi_{\frac{3}{2}} \\ -\psi_{-\frac{5}{2}} \end{bmatrix}$, and perform the unitary transformation: $|A_{1g}\rangle \rightarrow |A'_{1g}\rangle \equiv i|A_{1g}\rangle$, which allows us to rewrite \mathcal{H}_\perp in the standard notation

$$\mathcal{H}_\perp = \frac{\mathcal{J}_\perp^{21} - \mathcal{J}_\perp^{12}}{2} \eta_{q\mu}^\dagger \sigma_{\mu\nu}^+ \eta_{q\nu} S^- + h.c. + \mathcal{O} S^x,$$

with $q \in \{a, b\}$, $\mu, \nu \in \{\uparrow, \downarrow\}$. Here and in the following, repeated channel (q) and spin (μ, ν) indices are to be summed over; $\mathcal{O} = \mathcal{O}^\dagger$ contains only conduction electrons [25]; $\sigma^+ \equiv \sigma^x + i\sigma^y$ is composed of Pauli matrices; and $S^+ \equiv S^x + iS^y \equiv |A_{2g}\rangle\langle A'_{1g}|$; $S^z \equiv (|A_{2g}\rangle\langle A_{2g}| - |A'_{1g}\rangle\langle A'_{1g}|)/2$; $S^- \equiv S^{+\dagger}$; $\mathbb{1} \equiv |A_{2g}\rangle\langle A_{2g}| + |A'_{1g}\rangle\langle A'_{1g}|$.

Discussion. Channel symmetry is a consequence of time-reversal symmetry. The operator, $\mathcal{O} S^x$ is irrelevant around the 2CK fixed point (and marginal in the free fermion scaling regime), as shown either by NRG calculations or using conformal field theory results [14, 16]. It does not destroy the 2CK state, since it neither breaks channel symmetry, nor lifts the spin degeneracy. Thus we must have $\mathcal{J}_\perp^{12} \neq \mathcal{J}_\perp^{21}$ in order for overscreening to occur. This asymmetry comes up naturally e.g. if we start

off with a spherical symmetric Anderson Hamiltonian, perform the Schrieffer–Wolff transformation to arrive at a Kondo-type of interaction and then project to the crystal field states, $|A_{2g}\rangle$, $|A_{1g}\rangle$ at strong spin-orbit (i.e. jj) coupling, as described in refs. [1, 2, 14].

The diagonal part, \mathcal{H}_z cannot lead to non-Fermi liquid behavior by itself, but it can quite possibly destroy it. Channel symmetry is preserved by time-reversal symmetry. However, the level degeneracies are lifted by the crystal field, both between the $|4A_{2/1g}\rangle$ states and also in each screening channel between $\Gamma_{7u}^{(n)}$ electrons with different n ’s. The dangerous terms are

$$\mathcal{H}_{zi}^{rel} = \Delta_{imp} \eta_{q\mu}^\dagger \eta_{q\mu} S_z, \quad (3)$$

$$\mathcal{H}_{zc}^{rel} = \Delta_{cond} \eta_{q\mu}^\dagger \sigma_{\mu\nu}^z \eta_{q\nu} \mathbb{1}. \quad (4)$$

Both types of crystal field splittings are relevant around the 2CK fixed point with scaling dimension $\frac{1}{2}$ [14, 16], and present in \mathcal{H}_z with the amplitudes $\Delta_{imp} = (\mathcal{J}_z^{221} + \mathcal{J}_z^{111} - \mathcal{J}_z^{222} - \mathcal{J}_z^{112})/2$, and $\Delta_{cond} = (\mathcal{J}_z^{221} - \mathcal{J}_z^{111} + \mathcal{J}_z^{222} - \mathcal{J}_z^{112})/4$. In fact, they are the only possibilities for relevant perturbations, if channel symmetry is intact [16].

Thus for this model to exhibit 2CK scaling in some temperature range, Δ_{imp} and Δ_{cond} must fall below the Kondo scale, T_K . This necessarily requires fine-tuning, and the basic assumption of the $A_{2g} - A_{1g}$ scenario—and, as we show below, of any other doublet-ground state scenarios—is that this accidental degeneracy is responsible for the unique behavior of URu₂Si₂ among the large number of U-based heavy fermions. LDA+DMFT calculations for URu₂Si₂ are indeed consistent with this accidental degeneracy on the scale of T_K [6].

A local, z -directed magnetic field results in the following leading additions to the Hamiltonian

$$\mathcal{H}_{magi} \propto \mu_B i (S^+ - S^-)$$

$$\mathcal{H}_{magc} \propto \mu_B \sum_{J_z \in \{\pm\frac{3}{2}, \pm\frac{5}{2}\}} J_z \psi_{J_z}^\dagger \psi_{J_z} \mathbb{1}$$

for the two-singlet part and for the local conduction electrons, respectively. These terms have similar effect as $\mathcal{H}_{zi/c}^{rel}$. Namely, the impurity part, $\mathcal{H}_{zi}^{rel} + \mathcal{H}_{magi}$, amounts to an effective magnetic field (or crystal field splitting) pointing into other than the z -direction. The same holds true for the conduction electrons with the effective magnetic field/crystal field splitting being different in the two channels. Thus while \mathcal{H}_K is not identical to the 2CK Hamiltonian, it flows to the same fixed point when the relevant perturbations, which split apart the two different Γ_7 irreps, or the two local singlets, vanish; and the application of magnetic field thus breaks both the channel and the spin symmetry of the 2CK model.

Comparison with Other Scenarios. For the order of crystal field levels in URu₂Si₂, other scenarios have also been put forward in the literature. It turns out that the

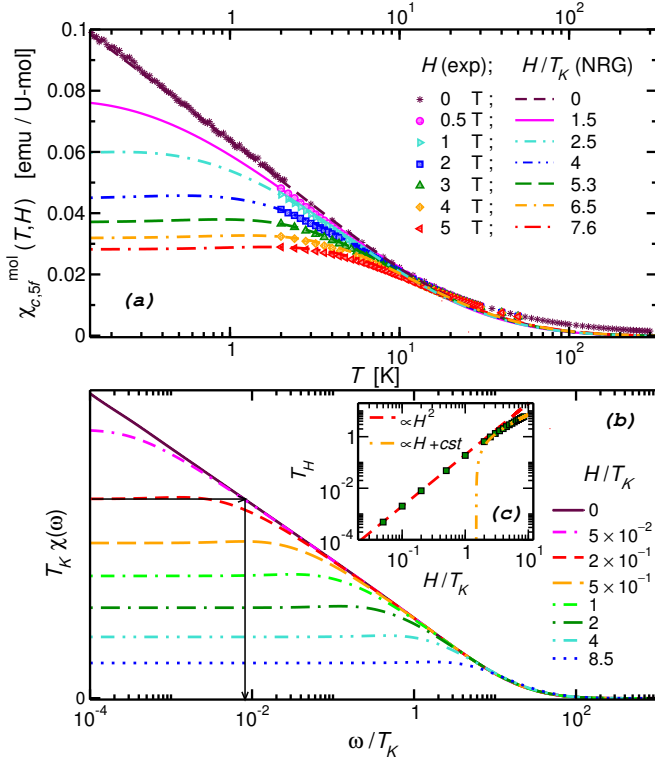


FIG. 1: (a) : Symbols: Molar susceptibility, $\chi_{c,5f}^{\text{mol}}$, of the 5f electrons in $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ at $x = 0.03$ as the function of temperature in magnetic fields between $H = 0$ and 5 T ($H \parallel c$). (a) – (b) : Curves: The local, dynamic susceptibility of the two-channel Kondo model in the presence of magnetic field, computed with density matrix-NRG at $T = 0$. (c) : The crossover scale, T_H (defined as the intersect of the low- ω and high- ω asymptotes of $\chi(\omega)$, see plot (b)) shows quadratic and linear H -dependence in the 2CK and local moment scaling regimes, respectively in good agreement with experiment; T_K , the crossover scale between the local moment and 2CK scaling regimes, is ≈ 1.3 K. Notice that the experimental data for $H = 0$ T can be equally well fitted with every NRG curve where $H \lesssim 0.2 T_K$.

structure of the effective low-energy Hamiltonian for any two quasi-degenerate states is rather similar to that of the two-singlet case considered above. This applies also to a proposed E_g (or Γ_5) doublet ground state [12, 17–19], formed by $|E_g x\rangle, |E_g y\rangle$. Fluctuations within this doublet can couple to two products of irreps: to $\Gamma_7 \otimes \Gamma_7$ and also to $\Gamma_7 \otimes \Gamma_6$. Importantly, the two different irreps play again the role of spin, while their Kramers indices, connected by time-reversal, play again the role of channel index in the 2CK language. If the two lower-lying irreps were degenerate, the spin symmetry of the 2CK model would be unbroken and 2CK scaling would occur. Since the degeneracy is approximate, the system will eventually flow to a Fermi liquid fixed point.

In the HO phase of URu_2Si_2 , the ref. [6] proposed order parameter, $\langle |A_{2g}\rangle \langle A_{1g}| \rangle$, is non-vanishing due to its real part which, in highest or-

der of the multipole expansion, contains the expectation value of the hexadecapolar A_{2g} tensor: $\left[(\hat{J}_x^2 - \hat{J}_y^2)(\hat{J}_x \hat{J}_y + \hat{J}_y \hat{J}_x) + (\hat{J}_x \hat{J}_y + \hat{J}_y \hat{J}_x)(\hat{J}_x^2 - \hat{J}_y^2) \right]$ [6]. However, the same reasoning can be repeated for $\langle |E_g x\rangle \langle E_g y| \rangle$, whose real part also contains this hexadecapolar ordering. These points are substantiated by the construction of the Hamiltonian for the E_g ground state in the supplementary material section.

Comparison with Experiment. It has long been recognized that χ_c , the (magnetic) dipole susceptibility of $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ along the c axis shows $\log T$ behavior at low- T (see refs. [12, 19] and Fig. 1) in accord with the 2CK descriptions corresponding to both scenarios. However, susceptibility and resistivity measurements find that the magnetic field (H) induced crossover scale to a Fermi liquid depends on H linearly, i.e. $T_H \propto H^\eta$ with $\eta = 1$, which does not agree with the $\eta = 2$ behavior corresponding to the 2CK scaling regime [13]. To make contact with these experiments, we solved the model, Eq. (1) by NRG, and confirmed that it indeed flows to the 2CK fixed point where \mathcal{OS}^x is irrelevant. Then we added a magnetic field, mimicked only by Eq. (3), to the 2CK model, and solved this model using an upgraded version of our density matrix-NRG code detailed in ref. [20]. The values of the magnetic field and the Kondo coupling were adjusted to fit the experimental data of refs. [12, 13].

Invoking ω/T scaling, we fitted the T -dependence of χ_c by the dynamic susceptibility of the 2CK model in magnetic field, as we trust our dynamic correlation functions (produced by the density matrix algorithm at $T = 0$) better than the thermodynamic quantities. Fig. 1 shows convincing agreement between theory and experiment apart from the small discrepancy for $T > 30$ K, i.e. for large energies where the resolution of NRG is limited. We obtained $T_K \approx 1.3$ K from the fit (see the caption of Fig. 1 for further details on T_K). This finding places the measurements in magnetic fields around the crossover region between the local moment and 2CK scaling regimes. In both regimes, scale invariance entails the hyperscaling relation, $\eta + \nu = 2$ with ν the critical exponent defined by $\chi \propto H^{-\nu}$. Thus for $H = 0$, the observed $\nu = 0$ gives $\eta = 2$, meaning that for T between 0.1 and 10 K, the system is in the 2CK scaling regime. In contrast, for $H = 1$ to 5 T, the experiments measure $\eta = 1$ resulting $\nu = 1$. Thus, we conclude, these magnetic fields in addition to the ubiquitous, relevant crystal field splitting, are (slightly) larger than T_K and the system flows directly from the local moment regime to a one-channel Kondo fixed point without traversing the 2CK scaling regime. In Fig. 1(a), the ratios of magnetic fields to T_K , fitting the susceptibility, further illustrate this point.

By taking a closer look at the specific heat coefficient in Fig. 2(a), we can reinforce these statements, and get another estimate for T_K . Two regimes for the given magnetic field values are clearly visible: The curves

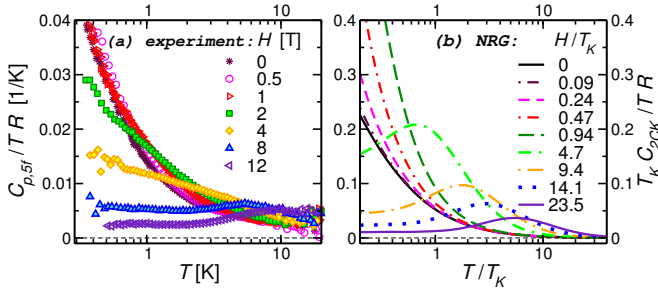


FIG. 2: (a) : The 5f electronic specific heat coefficient in units of R ($C_{p,5f}/TR$) of $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ at $x = 0.07$, in magnetic fields between 0 and 12 T, reproduced from ref. [19]. (b) : 2CK specific heat coefficient from NRG for different magnetic field values. The two sets of curves display the same trend. However there is a factor of ≈ 4 difference in the magnitudes (depending on the precise value of T_K). We ascribe this difference to experimental inaccuracy, as we observe a factor of ≈ 2 difference between the magnitudes of $C_{p,5f}/T$ for the same material published in refs. [12] and [19], respectively.

for $H = 0.5$ and 1 T slightly overshoot the curve at $H = 0$ T and low- T , in contrast to the curves for $H \geq 2$ T which exhibit a bump at around $T \approx H$. The rise of $\gamma \equiv C_{p,5f}/T$ for low-fields at low- T is reminiscent of the 2CK scaling regime, except that the measured T -dependence of γ at low- T for $H = 0$ is not quite logarithmic. These observations can be explained by the presence of an effective crystal field splitting, $0 < \Delta < T_K$, already at zero magnetic field, and placing T_K between 1 and 2 T. From the susceptibility fit we estimate: Δ is anywhere below about $0.2 T_K$ (c.f. Fig. 1(b)). These assertions are further confirmed by our NRG calculations for the specific heat coefficient (see Fig. 2(b) or Fig. 4 in ref. [21]). For $H > T_K$, the bumps at around $T \approx H$ correspond to the Schottky anomaly due to the Zeeman splitting between the two local states.

In the 2CK model, if $\Delta < T_K$, there is a non-Fermi liquid (NFL) region over $2 \log(\frac{T_K}{\Delta})$ decades, since the splitting induced crossover scale to a Fermi liquid depends on Δ quadratically. Susceptibility measurements find an NFL region over at least one decade, putting an upper bound on the ratio, $\Delta/T_K < 0.6$ and giving the conservative estimate: $T_K < 5$ T and $\Delta < 3$ T.

Conclusion. Motivated by recent findings on the electronic structure of URu_2Si_2 [6], we derived the Kondo coupling of localized hexadecapolar fluctuations to conduction electrons in tetragonal crystal field. The derivation can easily be adapted to arbitrary situations. The coupling has the form of the 2CK model plus relevant, spin symmetry breaking perturbations present even in magnetic zero field. The local degrees of freedom are symmetrically coupled to two different irreps of conduction electrons. Solving the model with NRG we showed that the hypothesis introduced in ref. [6] to describe the

hidden order in URu_2Si_2 can consistently account for the behavior of URu_2Si_2 in the dilute limit, $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ ($x \ll 1$). Nonetheless this behavior, while confirms that the material is strongly correlated, does not discriminate between different competing scenarios for the ground state-excited state sequence in this material. Since the two irreps of conduction electrons are not connected by symmetry, we expect a Fermi liquid to emerge at sufficiently low-energies. Hence the intermediate non-Fermi liquid regime, observed in URu_2Si_2 , is a result of an accidental degeneracy. This accidental degeneracy is responsible for the unique properties of this compound in the dilute and dense limits, among the hundreds of known U-based heavy fermion materials. We found that the scale of the crystal field splitting and the Kondo temperature is smaller in $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ ($x \ll 1$) than in URu_2Si_2 . The splitting between the two Γ_7 irreps should be sensitive to the conduction electron filling, and we expect it to be larger in $\text{La}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ [22] where clear Fermi liquid behavior is observed. In this context it is also worth pointing out that in $\text{Th}_{1-x}\text{U}_x\text{Ru}_2\text{Si}_2$ ($x \ll 1$), the resistivity follows an approximate $\log T$ behavior with a negative coefficient suggesting that a crossover to a Fermi liquid behavior takes place at sufficiently low temperatures. The study of the resistivity, however, will likely require a more realistic model for the diluted URu_2Si_2 , including all bands present in the solid; also a more sophisticated approach to calculating the resistivity in non-Fermi liquid quantum impurity models than the ones present in the literature [23]; and corrections to the very dilute limit as was done recently in the context of the NMR experiments [24].

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- [25] $\mathcal{O} \equiv \mathcal{J}_\perp^{12} \eta_{q\mu}^\dagger (\sigma_{\mu\nu}^+ + \sigma_{\mu\nu}^-) \eta_{q\nu}$
 $+ \mathcal{J}_\perp^{11} \left[\eta_{a\mu}^\dagger (\mathbb{1}_{\mu\nu} - \sigma_{\mu\nu}^z) \eta_{a\nu} - \eta_{b\mu}^\dagger (\mathbb{1}_{\mu\nu} - \sigma_{\mu\nu}^z) \eta_{b\nu} \right]$
 $+ \mathcal{J}_\perp^{22} \left[\eta_{a\mu}^\dagger (\mathbb{1}_{\mu\nu} + \sigma_{\mu\nu}^z) \eta_{a\nu} - \eta_{b\mu}^\dagger (\mathbb{1}_{\mu\nu} + \sigma_{\mu\nu}^z) \eta_{b\nu} \right].$

SUPPLEMENTARY MATERIAL FOR “HEXADECAPOLAR KONDO EFFECT IN URU₂SI₂?”

Kondo Hamiltonian for a Tetragonal E_g (or Γ_5) Doublet Ground State

The structure of the Hamiltonian for two singlets, $|A_{2g}\rangle, |A_{1g}\rangle$ and for any other two quasi-degenerate states has many common features. The proposed E_g (or Γ_5) doublet for the U ion ground state in Th_{1-x}U_xRu₂Si₂ ($x \ll 1$) is claimed to provide full symmetry protection for the 2CK state [12, 17–19]. We show that crystal field fine-tuning is needed in this case as well, to hit the 2CK scaling regime. On the vector space spanned by the E_g ground state doublet

$$\begin{aligned} |E_g x\rangle &\equiv \frac{1}{\sqrt{2}} [\cos \theta (|-1\rangle - |1\rangle) + \sin \theta (|-3\rangle - |3\rangle)], \\ |E_g y\rangle &\equiv \frac{i}{\sqrt{2}} [\cos \theta (|-1\rangle + |1\rangle) - \sin \theta (|-3\rangle + |3\rangle)], \end{aligned}$$

we have four independent operators defined e.g. as $\mathbb{1}_E \equiv |E_g x\rangle \langle E_g x| + |E_g y\rangle \langle E_g y|$, $\sigma_E^x \equiv i (|E_g x\rangle \langle E_g y| - |E_g y\rangle \langle E_g x|)$, $\sigma_E^z \equiv |E_g x\rangle \langle E_g x| - |E_g y\rangle \langle E_g y|$ and $\sigma_E^y \equiv |E_g x\rangle \langle E_g y| + |E_g y\rangle \langle E_g x|$. They transform as A_{1g} , A_{2g} , B_{1g} and B_{2g} tensors of D_{4h} , respectively [15]. In the Kondo limit, these operators can appear in the Hamiltonian only in certain combinations with the conduction electrons [14]. Namely, the B_{1g} and B_{2g} tensors can only couple to products of Γ_6 and Γ_7 electrons following the rule: $\Gamma_{6u} \otimes \Gamma_{7u} = B_{1g} \oplus B_{2g} \oplus E_g$, i.e.

$$\begin{aligned} \mathcal{H}_{\perp}^{E_g} &= i \sum_{m=1}^2 \mathcal{J}_{\perp B_2}^m \left(\Psi_{\Gamma_6^{(1)+}}^{\dagger} \Xi_{\Gamma_7^{(m)-}} + \Psi_{\Gamma_6^{(1)-}}^{\dagger} \Xi_{\Gamma_7^{(m)+}} \right) \sigma_E^x + \sum_{n,m=1}^2 \mathcal{J}_{\perp A_2}^{nm} \left(\Psi_{\Gamma_7^{(n)+}}^{\dagger} \Xi_{\Gamma_7^{(m)-}} + \Psi_{\Gamma_7^{(n)-}}^{\dagger} \Xi_{\Gamma_7^{(m)+}} \right) \sigma_E^y \\ &\quad + \mathcal{J}_{\perp A_2} \left(\Psi_{\Gamma_6^{(1)+}}^{\dagger} \Xi_{\Gamma_6^{(1)-}} + \Psi_{\Gamma_6^{(1)-}}^{\dagger} \Xi_{\Gamma_6^{(1)+}} \right) \sigma_E^y + h.c., \\ \mathcal{H}_z^{E_g} &= \sum_{m=1}^2 \mathcal{J}_{z B_1}^m \left(\Psi_{\Gamma_6^{(1)+}}^{\dagger} \Xi_{\Gamma_7^{(m)-}} - \Psi_{\Gamma_6^{(1)-}}^{\dagger} \Xi_{\Gamma_7^{(m)+}} \right) \sigma_E^z + \sum_{n,m=1}^2 \mathcal{J}_{z A_1}^{nm} \left(\Psi_{\Gamma_7^{(n)+}}^{\dagger} \Xi_{\Gamma_7^{(m)-}} - \Psi_{\Gamma_7^{(n)-}}^{\dagger} \Xi_{\Gamma_7^{(m)+}} \right) \mathbb{1}_E \\ &\quad + \mathcal{J}_{z A_1} \left(\Psi_{\Gamma_6^{(1)+}}^{\dagger} \Xi_{\Gamma_6^{(1)-}} - \Psi_{\Gamma_6^{(1)-}}^{\dagger} \Xi_{\Gamma_6^{(1)+}} \right) \mathbb{1}_E + h.c., \end{aligned}$$

with arbitrary real couplings. Again, each allowed term describes a 2CK screening process, and channel symmetry is guaranteed by time-reversal symmetry. One apparent difference from the two-singlet case is that Γ_{6u} conduction electrons combined with Γ_{7u} 's can also participate in real 2CK screening processes. Besides there remains also the possibility of the two Γ_{7u} 's forming the two screening channels. Once we single out the two lowest-lying channels, the two cases become very similar in that the diagonal processes for the E_g ground state also include a relevant splitting between the different crystal field channels of conduction electrons. Thus an E_g doublet ground state does not enjoy level degeneracy protection, and in this respect, it is not distinguished from other, two-singlet ground state scenarios in tetragonal symmetry. Full protection of the 2CK state can be achieved in a setting where cubic symmetry merges the Γ_6 and Γ_7 representation into a Γ_8 quartet as in Cox's original proposal [1].